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## MAGNESIUM-ZIRCONIUM ALLOYING

FIELD OF THE INVENTION

- 5 The present invention relates to the addition of zirconium to pure magnesium or magnesium alloys and to the preparation of magnesium-zirconium (Mg-Zr) alloys, including Mg-Zr master alloys.

10 BACKGROUND TO THE INVENTION

- Zirconium is a potent grain refiner for magnesium alloys which contain negligible amounts of elements with which zirconium forms stable compounds, such as Al, Si, Fe, Ni, Co, Sn and Sb. Zirconium additions of about 1% by weight to such magnesium alloys can readily cause the grain size to decrease by 80% or more under normal cooling rates. The exceptional grain refining ability makes zirconium an important alloying element for magnesium alloys that are not based on alloying with Al and Si. For example, zirconium containing Mg-RE-Zn alloys such as EZ33 (Mg-3.3RE-2.7Zn-0.6Zr) and ZE41 (Mg-1.2RE-4.2Zn-0.7Zr) offer a specific combination of elevated temperature and room temperature properties which are not achievable with the Mg-Al-Zn alloys.

- The solubility of zirconium in molten pure magnesium is approximately 0.6%, which slightly increases with increasing melt temperature. It has been reported that the most characteristic feature of the microstructure of a magnesium alloy that contains more than a few tenths per cent soluble zirconium is the zirconium-rich cores that exist in most of the magnesium grains. These zirconium-rich cores are believed to be the products of peritectic solidification. In order to achieve excellent grain refinement in commercial production, it is desirable to dissolve the full zirconium content (ie, about 0.6%) in a

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ART 34 AND 35 magnesium melt.

Over the decades various approaches to introducing zirconium into molten magnesium have been explored, including:

- (a) alloying with different forms of zirconium metal;
- (b) alloying with zirconium sponge;
- (c) alloying with Zn-Zr master alloys;
- 10 (d) alloying with  $ZrO_2$ ;
- (e) alloying with various zirconium halides or complex halides or a mixture of halides and/or complex halides with different salts such as NaCl, KCl,  $BaCl_2$ , NaF, KF, etc; and
- 15 (f) alloying with Mg-Zr master alloys.

The advantages and disadvantages of each of these approaches have been discussed in detail by Saunders and Strieter (W. P. Saunders and F. P. Strieter, "Alloying Zirconium to Magnesium", Transactions of the American Foundrymen's Society, 1952, Vol. 60, pp. 581-594) and Emley (E. F. Emley, "Principles of Magnesium Technology", Pergamon Press, Oxford, 1966, pp. 127-155). Since about 1960, only Mg-Zr master alloys have been in widespread commercial use as sources of zirconium for alloying with magnesium. These Zr-rich Mg-Zr master alloys are made by chemical reduction by magnesium of salt mixtures based on zirconium fluorides or zirconium chlorides. Both types of master alloy are essentially the same and contain about one third their weight of zirconium. One of them, developed by Magnesium Elektron Ltd (MEL) in about 1945 via chemical reduction of a complex zirconium fluoride with molten magnesium, has been long known as Zirmax (trade mark). A similar type of Mg-Zr master alloy was developed in the United States based on a chloride salt reduction process.

5 the zirconium is present as various sizes of zirconium  
particles (mostly in the range of submicron to 10  $\mu\text{m}$ ) in a  
magnesium matrix.

10 source of zirconium for zirconium-containing magnesium  
alloys, alloying with various forms of zirconium metal  
were investigated.

15 powder to magnesium in 1947 (V. F. Sauerwald, "Dus  
Zustandsdiagram Magnesium-Zirkonnium", Zeitschrift fur  
anorganische Chemie., 1947, Band 255, pp. 212-220). He  
added 5 wt% zirconium metal powder to magnesium under an  
argon atmosphere at various temperatures between 680 and  
20 1100°C. Soluble zirconium contents exceeding 0.5 wt%  
(samples were digested in HCl acids) were obtained at all  
temperatures tested. In the same year, Ball reported work  
(C. J. P. Ball, "Metallurgia", 1947, Vol. 35, pp. 125-  
129; 211) stating that metallic zirconium dissolves in  
25 magnesium under an argon atmosphere at 900-1100 °C but that  
it was a difficult and costly process. Operating at such  
temperatures is not commercially feasible in view of  
vaporisation of magnesium. Emley reported in 1948 (E. F.  
Emley, "Discussions of the Faraday Society", 1948-49, Vol.  
30 47, No. 4, pp. 219) that as zirconium metal powder is  
expensive and highly inflammable, it is natural to  
consider the possibility of alloying by a reducible  
zirconium compound.

35 In 1952, Saunders and Strieter reported their  
investigations in which different forms of metallic  
zirconium, (ie, zirconium sponge, fused zirconium, iodide-

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smaller than 3 microns, it can be readily suspended in a magnesium melt at the same temperature.

Chambers Science and Technology Dictionary (1991) defines  
5 "passivity" as "Lack of response of metal or mineral  
surface to chemical attack such as would take place with a  
clean, newly exposed surface. Due to various causes,  
including insoluble film produced by ageing, oxidation, or  
contamination; run-down of surface energy at discontinuity  
10 lattices; adsorbed layers..." Throughout this  
specification, the terms "depassivate", "depassivated" and  
"depassivating" are to be understood to have meanings  
derived from the foregoing definition of "passivity".

#### 15 SUMMARY OF THE INVENTION

In a first aspect, the present invention provides a method  
for treating zirconium metal, the method comprising  
chemically depassivating the zirconium metal. The  
20 zirconium metal is preferably zirconium sponge with the  
method forming treated zirconium sponge. The zirconium  
sponge may be chemically depassivated by treatment with a  
source of fluoride ions. The source of fluoride ions may  
be hydrofluoric acid. The source of fluoride ions may be  
25 a mixture of hydrofluoric acid and nitric acid.

The hydrofluoric acid preferably has a concentration  
between 0.10% and 50.0%, more preferably between 0.50% and  
5.0%, and most preferably between 1.5% and 2.5%, with the  
30 acid concentrations calculated as shown later in this  
specification. These acid concentration ranges correspond  
respectively to 0.05 - 50.0 molar, 0.25 - 2.63 molar and  
0.76 - 1.28 molar, which may be rounded to 0.05 - 50.0  
molar, 0.25 - 3.0 molar and 0.75 - 1.5 molar.

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